Temporally two-dimensional fifth-order Raman scattering on intermolecular vibrations in CS2/pentane binary mixtures

Steffen, T; Nakashima, S.; Duppen, K.

Published in:
Laser Chemistry

DOI:
10.1155/1999/18612

Laser Chem., 1999, Vol. 19, pp. 91–96
Reprints available directly from the publisher
Photocopying permitted by license only

TEMPORALLY TWO-DIMENSIONAL FIFTH-ORDER RAMAN SCATTERING ON INTERMOLECULAR VIBRATIONS IN CS_2/PENTANE BINARY MIXTURES

THOMAS STEFFEN, SATORU NAKASHIMA*
and KOOS DUPPEN†

Ultrafast Laser and Spectroscopy Laboratory, Dept. of Chemical Physics, Mat. Science Center, University of Groningen, 9747 AG Groningen, The Netherlands

(Received 7 April 1997)

Third- and fifth-order impulsive stimulated Raman scattering experiments are performed to study low-frequency intermolecular vibrations in CS_2/pentane binary mixtures. The changes of the optical Kerr effect response cannot be assigned unequivocally to a single microscopic process. In particular, the homogeneous and inhomogeneous line broadening mechanisms cannot be determined. Temporally two-dimensional Raman scattering experiments indicate that the correlation time of fluctuations of the intermolecular potential decreases upon dilution. The experimental results give evidence of strong coupling between the ultrafast coherent vibrations and the slow reorientational diffusion.

Keywords: Raman scattering; Kerr effect; intermolecular vibrations

I. INTRODUCTION

The microscopic structure and dynamics in liquids are of great importance for our understanding of chemical reactions in solutions [1]. Nonresonant Raman experiments such as the optical Kerr effect [2] and transient grating scattering [3] are suitable tools to study intermolecular motions in condensed phases. These techniques yield the total spectrum, but are incapable to separate homogeneous and

*Permanent address: Dept. of Chemistry, Osaka University, Toyonaka 560, Japan.
† Corresponding author.

inhomogeneous line broadening mechanisms [4]. The temporally two-dimensional Raman experiment, proposed a few years ago by Tanimura and Mukamel [4], surpasses the conventional Raman methods by providing information on the time scales of the microscopic fluctuations. Very recently, this experiment, that is depicted schematically in Figure 1, was reported by a number of groups [5–7]. Here we present third- and fifth-order results for carbon disulfide (CS_2)/pentane binary mixtures.

II. EXPERIMENTAL

The experiments were performed using 50 fs laser pulses at 620 nm with a repetition rate of 8.8 kHz and a pulse energy of 1 μJ. The Kerr effect setup was similar to that of McMorrow and coworkers [2], the fifth-order setup was identical to that of Ref. [6b]. The experimental details will be published elsewhere [8].

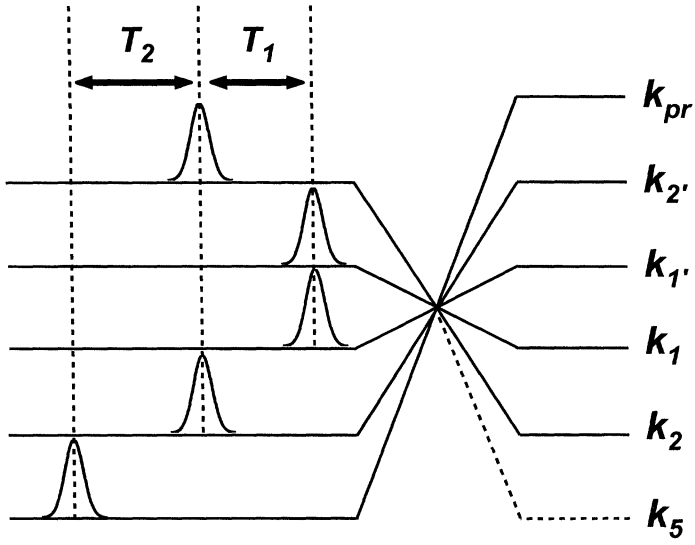

FIGURE 1 Principle of the temporally two-dimensional Raman scattering experiment. Two subsequent pulse pairs, separated by a variable delay T_1, are followed after second variable delay T_2 by the probe pulse that generates a fifth-order signal in the direction $\mathbf{k}_5 = \mathbf{k}_1 - \mathbf{k}_{1'} + \mathbf{k}_2 - \mathbf{k}_{2'}$.

III. THIRD-ORDER EXPERIMENTS

The optical Kerr effect response of neat CS_2 is shown in Figure 2a. It shows three distinct dynamic features: a pulse-limited peak at zero delay due to electronic hyper-polarizability, a slowly decaying tail that is assigned to reorientational diffusion, and a large contribution at short delays exhibiting a finite rise and decay time that is attributed to inertial librational motion [2a]. The spectral changes upon dilution become more transparent after subtracting the slow diffusive decay and deconvoluting the data in frequency domain [2b]. The spectra, shown in Figure 2b, narrow and shift to lower frequencies as pentane is added. McMorrow *et al.* [2c] concluded from a similar observation that the inhomogeneous width and the center frequency of the librations decrease. However, these modifications may also be due to decreasing homogeneous decay rates or other scattering mechanisms such as collision- and interaction-induced effects [9]. The third-order experiment does not provide sufficient information to unambiguously establish the microscopic origin of the observed spectral changes.

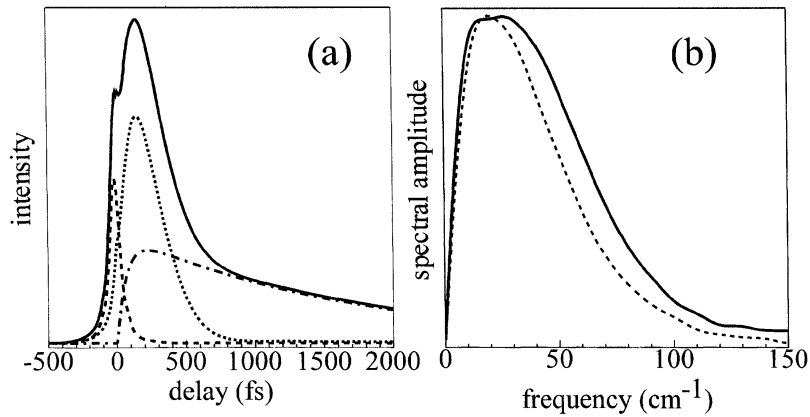

FIGURE 2 (a) The optical Kerr response of CS_2 (solid line). Three distinct contributions can be recognized: (i) A pulse-limited response at zero delay (dashed), (ii) a delayed nuclear response with subps rise and decay times (dotted) and a slowly decaying exponential component (dashed dotted); (b) Frequency domain representation of the deconvoluted material response of pure CS_2 (solid line) and a 50 vol.% mixture of CS_2 and pentane (dashed). Upon dilution the spectrum narrows and shifts to lower frequencies.

IV. FIFTH-ORDER EXPERIMENTS

In order to characterize the microscopic processes that cause the total line width, fifth-order Raman scattering measurements were performed. The 2-D Raman response, given in Figure 3, shows different dynamics along the two time variables. The signal as function of T_2, depicted in Figures 3a and b, is governed by the librations. When the other time variable T_1 is varied, the 2-D Raman response shows a sharp peak at zero delay, followed by a prominent tail that decays with the time constant of the rotational diffusion (see Fig. 3c). The signal shape along T_2 changes when T_1 is increased: the decay slows down and the maximum slightly shifts. However, we do not observe clear echo-type behaviour, indicating that the degree of inhomogeneous broadening of the librations is quite small [6b].

Upon dilution in pentane these T_1-dependent features of the response along T_2 become less pronounced. At early T_1 the signal decay in the mixtures is slower when compared to the neat liquid. When T_1 is increased, the response of the mixture shows only small changes and the decays of the neat liquid and the mixture are almost

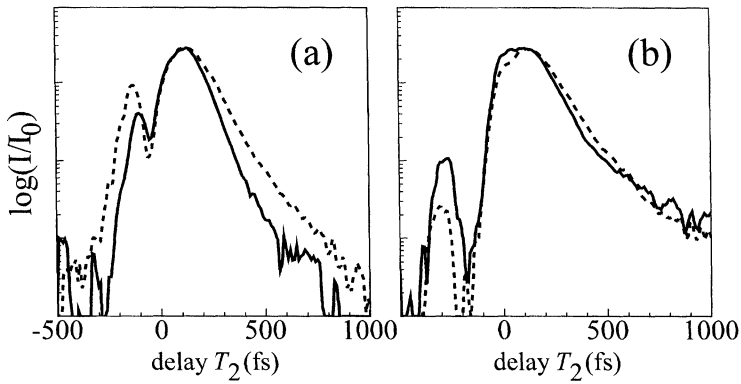

FIGURE 3 (a) Fifth-order Raman signal of pure CS_2 (solid line) and a 50 vol.% mixture of CS_2 and pentane (dashed) along T_2 for T_1 = 100 fs; (b) *dito* for T_1 = 300 fs. At small T_1 the decay is faster in the neat liquid, but this difference vanishes when T_1 is increased. As T_1 is increased, the traces along T_2 become broader. In the mixture this feature is less pronounced, which indicates that the inhomogeneous broadening decreases upon dilution; (c) Fifth-order signal of neat CS_2 (solid line) along T_1 for T_2 = 170 fs. Next to a sharp peak at zero delay the signal shows a long exponential tail (dashed) that decays with a time constant of 800 fs as is shown in the inset.

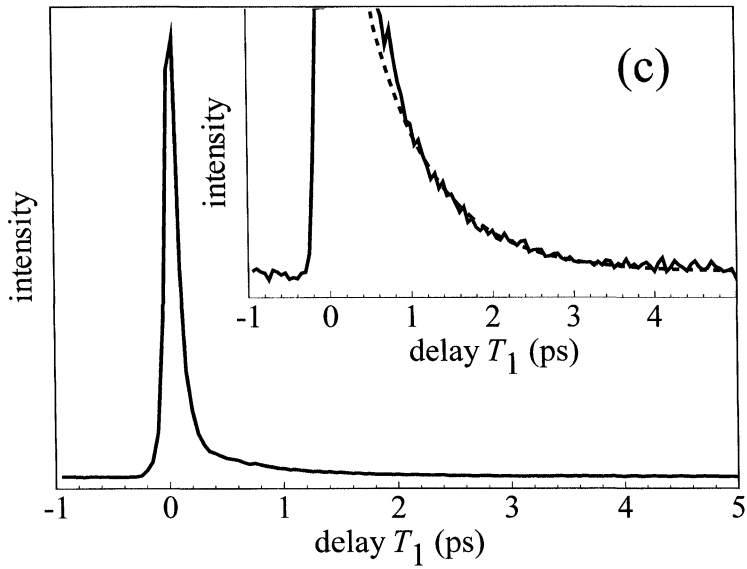

FIGURE 3 (Continued).

identical. This might indicate that the correlation time of the fluctuations of the intermolecular potential is getting shorter with decreasing CS_2 concentration [8].

However, the Tanimura–Mukamel model cannot account for the full 2-D information content obtained from the experiment. In particular, the different dynamics along the two time variables is not explained satisfactory. Therefore, it is not straightforward to determine the inhomogeneity of the intermolecular vibrations from the fifth-order experiment. The results indicate that the inertia-limited motions on a subps time scale and the slow diffusive motion are strongly coupled [10].

Acknowledgements

Miss Nicole Meinders is acknowledged for her assistance in the OHD–OKE measurements. The investigations were supported by the Netherlands Foundations for Chemical Research (SON) and Physical

Research (FOM) with financial aid from the Netherlands Organization for the Advancement of Science (NWO).

References

[1] Fleming, G. R. and Hänggi, P., Eds. (1993). *Activated Barrier Crossing* (World Scientific, Singapore).
[2] (a) McMorrow, D., Lotshaw, W. T. and Kenney-Wallace, G. A. (1988). *IEEE J. Quantum Electron.*, **QE-24**, 443; (b) McMorrow, D. and Lotshaw, W. T. (1991). *J. Phys. Chem.*, **95**, 10395; (c) McMorrow, D., Thantu, N., Melinger, J. S., Kim, S. K. and Lotshaw, W. T. (1996). *J. Phys. Chem.*, **100**, 10389.
[3] (a) Ruhman, S., Williams, L. R., Joly, A. G. and Nelson, K. A. (1987). *J. Phys. Chem.*, **91**, 2237; (b) Waldman, A., Banin, U., Rabani, E. and Ruhman, S. (1992). *J. Phys. Chem.*, **96**, 10842.
[4] Tanimura, Y. and Mukamel, S. (1993). *J. Chem. Phys.*, **99**, 9496.
[5] (a) Tominaga, K. and Yoshihara, K. (1995). *Phys. Rev. Lett.*, **74**, 3061; (b) Tominaga, K. and Yoshihara, K. (1996). *J. Chem. Phys.*, **104**, 1159; (c) *ibid.*, **104**, 4419 (1996).
[6] (a) Steffen, T. and Duppen, K. (1996). *Phys. Rev. Lett.*, **76**, 1224; (b) Steffen, T. and Duppen, K. (1997). *J. Chem. Phys.*, **106**, 3854.
[7] Tokmakoff, A. and Fleming, G. R. (1997). *J. Chem. Phys.*, **106**, 2569.
[8] Steffen, T., Nakashima, S. and Duppen, K., manuscript in preparation.
[9] Steffen, T., Meinders, N. A. C. M. and Duppen, K. (1998). *J. Phys. Chem. A*, **102**, 4213.
[10] Steffen, T. and Duppen, K. (1998). *Chem. Phys. Lett.*, **290**, 229.